
V.10 Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life

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Objectives

- Determine the sensitivity of solid oxide fuel cell (SOFC) performance to trace level contaminants present in coal-derived gas streams.
- Assess the catastrophic damage risk and long-term cumulative effect of trace level contaminants.
- Assess the life expectancy of solid oxide fuel cell systems fed with coal-derived gas streams.

Accomplishments

- Conducted a critical review of literature which indicated that Ni-cermet based SOFCs are vulnerable to degradation in the presence of contaminants that are expected to be present in a coal-derived fuel gas stream.
- Performed thermodynamic calculations to determine the speciation of various contaminants at SOFC operating temperatures.
- Assembled and tested several Ni-cermet SOFCs under varying conditions with select contaminants (HCl, CH₃Cl, and volatile species of As, P, Hg, Zn, Cd, and Sb) in a simulated coal-derived gas stream.

Introduction

SOFCs have high fuel-to-electricity conversion efficiency, environmental compatibility (low NO_x production), and modularity. They operate in the temperature range 700-1,000°C and can use fuel streams

containing both H₂ and CO. Thus, they are ideal candidates to be integrated with a gas stream from an advanced coal gasifier. However, impurities containing virtually every element in the periodic table are present in coal (Clarke and Sloss, 1992) and many become constituents of coal-derived gas. The distribution of trace level contaminants between gaseous and solid phases depends on the individual gasification processes. The contaminants associated with the gaseous phase have deleterious effects on the performance and lifetime of coal-derived gas fed SOFCs.

The well-known impurities in the coal-derived gas stream include H₂S, NH₃, and HCl vapors; volatile metals such as Zn, Cd, and Hg; and metalloids such as As, P, and Sb; and transition metals such as Ni, Cr, and V, and Mn (Pigeaud and Helble, 1994). Some of these contaminants such as H₂S are removed by several methods. This project addresses the effect of the key impurities such as HCl, methyl chloride, zinc, mercury, arsenic, phosphorous on the efficiency and lifetime of SOFCs.

Approach

The research project includes a literature review, thermodynamic calculations, and a comprehensive experimental and analytical study to assess the impact of trace contaminants on SOFC performance.

1. A review of the scientific literature provided a preliminary assessment of the effect of trace level contaminants on the performance of the SOFC.
2. Thermodynamic equilibrium calculations allowed the identification of the chemical nature of the trace contaminants as they pass through the gas cleanup system from the coal gasifier and enter the SOFC anode.
3. A well-defined experimental program was designed to substantiate the preliminary assessment based on thermodynamic calculations and literature data.

In the second year of the project, the SOFC anodes (Ni-cermet) were exposed to a simulated coal gas containing individual contaminants at the operating temperature range of the SOFC (700 to 850°C) for an extended period of time. During such exposure, the electrical performance of the SOFC is monitored to determine the performance degradation. After the exposure period, the anodes are analyzed for the accumulation of the contaminants.

Results

The results of the literature review and thermodynamic calculations were summarized in the 2006 annual report. Also included in that report was the performance of the SOFC during exposure to a simulated coal-derived gas containing ~40 ppm of HCl or CH₃Cl vapors. In Table 1 of this report, the performance of the SOFC on exposure to other contaminants such as As, P, Hg, Zn, Cd, and Sb is summarized.

The various contaminants in the coal-derived gas exiting the gasifier can be removed by several well-known processes such as Selexol or Rectisol. These processes also remove essentially all the fly ash particles from the gas stream. Many gaseous contaminants are also reduced to sub-ppm levels. Hence, long-term data (>1,000 h) of SOFC performance were obtained with selected impurities at sub-ppm levels. However, during upset conditions, the impurity levels may be higher than those found at steady-state operating conditions. Thus, short-term data (~100 h) were also collected with impurity levels ranging from 5 to 40 ppm.

For short and long term tests, solid oxide Ni-cermet fuel cell samples from InDec B. V., Netherlands (4.5 cm² active area) were used. They have an electrolyte layer of dense yttria-stabilized zirconia (YSZ) of 4 to 6 μm in thickness, porous anode layer of 5 to 10 μm, porous anode support layer of 520 to 600 μm, and a porous lanthanum strontium manganite - yttria-stabilized zirconia (LSM-YSZ) cathode layer of 30 to 40 μm thick. The cells were operated at 750° to 850°C with syngas (30% CO, 30.6% H₂, 11.8% CO and 27.6% H₂O) under 1 A load. After stabilization in the simulated coal-derived gas mixture without known contaminants, the cell was exposed to a low level of the select contaminant

(0.5 to 50 ppmv) by adding them into the simulated gas mixture.

Figure 1 shows the performance of a cell on exposure to the simulated coal-derived gas stream containing 7 ppm mercury vapor. Even at this high level, Hg vapor did not have an effect on the power density of the cell. Similar results were obtained at 750 and 850°C both at 0.18 and 7 ppm levels. Because of its volatility, Hg vapor is difficult to remove from the gas stream and the results from these tests show that Hg vapor need not be reduced to sub-ppm levels for use in the SOFC.

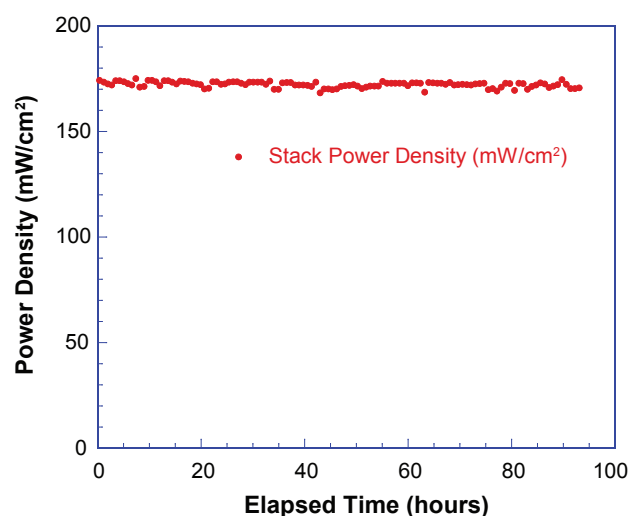


FIGURE 1. The Variation of the Power Density of a Cell at 800°C during Exposure to Simulated Coal-Derived Gas Containing 7 ppm Hg Vapor

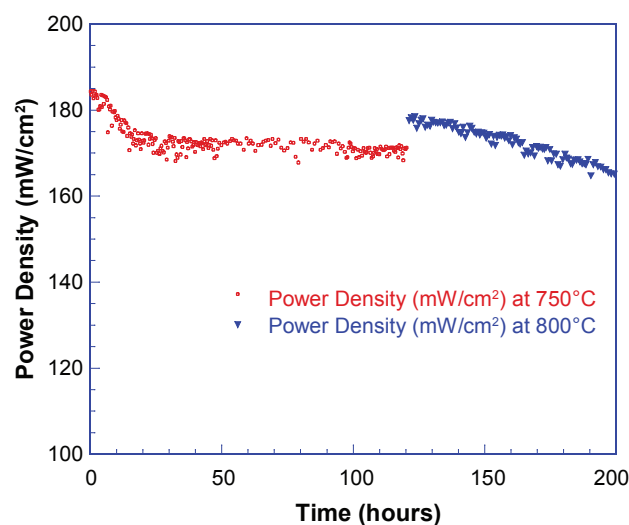


FIGURE 2. The Variation of the Power Density of a Cell at 750° and 800°C during Exposure to Simulated Coal-derived Gas Containing 40 ppm HPO₂ Vapor

TABLE 1. Effect of Trace Level Impurities on SOFC Output Power

Contaminant	Exposure Level	Observed Degradation (%) after 100 h at		
		750°C	800°C	850°C
HCl(g)	40	<1	<1	
Hg(g)	7	<1	<1	
Sb (SbO(g))	8	<1	<1	<1
Zn(g)	10		<1	<1
Cd (g)	5		<1	8
CH ₃ Cl (g)	40		<1	4
As (As ₂ (g))	10	10	15	
P (HPO ₂ (g))	40	7.5	10	

Figure 2 shows the performance of a cell on exposure to a phosphorous-containing vapor ($\text{HPO}_2(\text{g})$). Thermodynamic equilibrium calculations showed that in the presence of steam and the temperature range 750 to 850°C, phosphorous compounds such as PH_3 that are stable at near-ambient temperatures will be converted to $\text{HPO}_2(\text{g})$. At high levels, the vapor phase phosphorous compound appears to have a deleterious effect on the output power of the SOFC. We are planning to conduct tests at sub-ppm levels with PH_3 in the near future to establish the tolerance limit.

Volatile arsenic compounds such as AsH_3 may also be present at trace levels in the coal-derived gas even after treatment with Selexol. Short-term (100 h) tests with $\text{As}_2(\text{g})$ showed that the As compounds at a level of 10 ppm also degrade the SOFC performance at 750° and 800°C. However, when the concentration of As vapor (AsH_3) was reduced to 0.5 ppm, no degradation was observed even after 1,000 h (Figure 3). Additional tests are underway to determine the tolerance limit of SOFC for AsH_3 .

The short term tests indicated that many of the potential trace level impurities do not have a significant effect on the output power density in the temperature range 750° to 850°C even at relatively high levels of the impurity. However, volatile impurities such as As and P

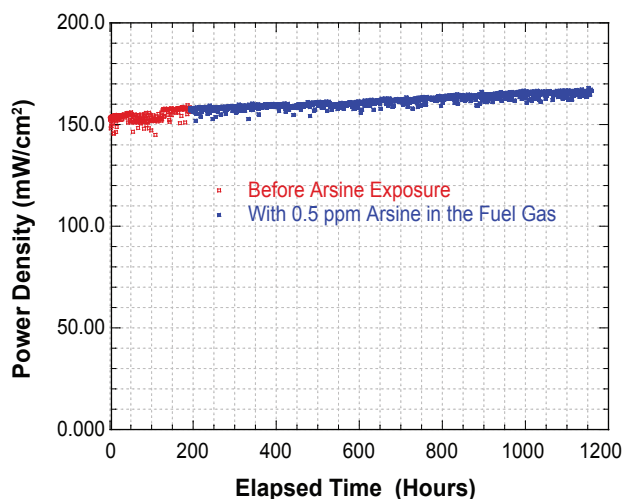


FIGURE 3. The Variation of the Power Density of a Cell at 750°C during Exposure to Simulated Coal-Derived Gas Containing 0.5 ppm AsH_3 Vapor

vapor compounds exhibited observable degradation in the 100 h tests.

Conclusions and Future Directions

- Several potential trace level contaminants (HCl, Sb, Zn, and Hg) at relatively high levels (5 to 40 ppm) do not have a significant effect on the performance of SOFC coupons under short-term exposure conditions.
- Volatile species of As and P at relatively high levels (10 and 40 ppm, respectively) appear to degrade the power output of SOFC in 100 h.
- AsH_3 at 0.5 ppm level did not degrade the performance of an SOFC coupon even after 1,000 h of exposure indicating that this contaminant when present at sub-ppm levels may not have a significant effect.
- In future experiments, we will expose SOFC coupons to simulated coal-derived gas streams containing several contaminants (H_2S , PH_3 , AsH_3) and determine their effect on long-term performance (1,000 h) of the cells.

FY 2007 Publications/Presentations

1. Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life, Quarterly Technical Progress Report 2 covering the period October 1, 2006 through December 31, 2006.
2. Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life, Paper presented at the 7th Annual SECA Review Meeting, Philadelphia, September 12-14, 2006.
3. Effect of Coal Contaminants on Solid Oxide Fuel System Performance, Presentation at West Virginia University Symposium, March 21, 2007.

References

1. Clarke, L. B. and L. L. Sloss (1992). Trace Elements – Emissions from Coal Combustion and Gasification, IEA Coal Research, London.
2. Pigeaud, A. E., and J. J. Helble (1994). “Trace Species Emissions for IGFC,” Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting, Eds. H. M. McDaniel, R. H. Stauby, and V. K. Venkataraman, DOE/METC-94/1008.